Orthogonal self-assembly of surfactants and hydrogelators: towards new nanostructures

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Self-assembly of small molecular components holds great promises as a bottom-up approach for nano-objects, but functionality of the resulting nanostructures can by far not compete with the sophisticated systems provided by nature. Surfactants, for instance, can lead to a great diversity of aggregates and mesophases (micelles, vesicles, cubic phases…), but with a level of complexity and functionality that still remains limited. Just like in nature, to increase the level of complexity in self-assembling systems, a straightforward approach consists in making use of multiple components that can display orthogonal self-assembly –i.e. the independent formation of two supramolecular structures each with their own characteristic within a single system. More precisely, we have associated surfactants with low-molecular weight hydrogelators: these molecules, based on cyclohexyl-tris-amino acid, can also self-assemble in one direction through the establishment of H-bonds, leading to the formation of a fiber network and consequently macroscopic gels. Work on mixing behavior of surfactants and various gelators have shown the independent formation of a fibrillar network with encapsulated spherical micelles, Figure 1. In order to produce even more complex nanostructures, this approach has been extended to worm-like micelles that can lead to viscoelastic gels, due to their entanglement. Interestingly, the formation of interpenetrating networks, with original and tuneable rheological properties, has been evidenced by cryo-TEM [1]. Screening of various gelators with vesicle-forming surfactants also revealed that most combinations display orthogonal self assembly, Figure 1. Vesicles were indeed successfully incorporated in a highly responsive network of fibers, without any significant disturbance of these two supramolecular structures. By mean of fluorescent spectroscopy, the stability of these encapsulated vesicles with respect to fusion and leakage has also been investigated. This last example has been exploited to successfully develop liposomes with an encapsulated self-assembling hydrogel ("gellosomes") [1]. The high responsive character of the gelator makes it very interesting as a mimic of cytoskeleton and it is expected that this new type of nanostructure might be of great interest in drug delivery.

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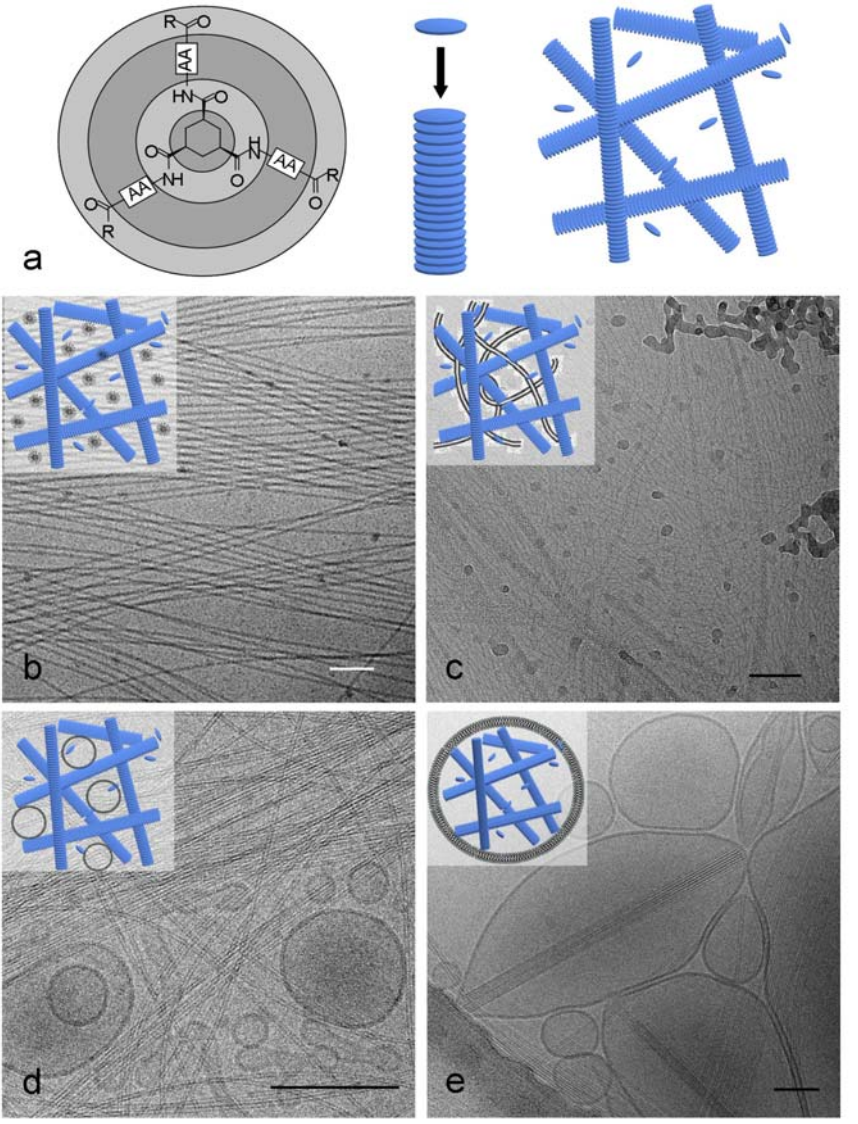

Figure. 1 Cyclohexyl-tris-amino acid based hydro-gelator molecules have alternating hydrophilic and hydrophobic regions and can assemble into fibrillar networks by H-bonding (a). Cryo-electron microscopy showed orthogonal self-assembly with surfactant micelles (b), worm-like micelles (c) and phospholipid vesicles (d). Formation of "gellosomes", vesicles with encapsulated gel network (e). Bar 100 nm.